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**DEVELOPMENT OF A
HETEROGENEOUS LAMINATING
RESIN SYSTEM**

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SUMMARY

This contractual effort was directed towards the study of factors which effect the impact resistance of laminating resin systems and yet retain equivalent performance with the conventional 450K (350°F) curing epoxy matrix systems in other areas. Formulation work was conducted on two systems, an all-epoxy and an epoxy/bismaleimide, to gain fundamental information on the effect formulation changes have upon neat resin and composite properties. The all-epoxy work involved formulations with various amounts and combinations of eight different epoxy resins, four different hardeners, fifteen different toughening agents, a filler, and a catalyst. The epoxy/bismaleimide effort involved formulations with various amounts and combinations of nine different resins, four different hardeners, eight different toughening agents, four different catalysts, and a filler. When a formulation appeared to offer the proper combination of properties required for a laminating resin (e.g. melt impregnable, reasonable working time, tack, etc.), Celion 3K-70P fabric was prepregged. Initial screening tests on composites primarily involved Gardner type impact and measurement of short beam shear strengths under dry and hot/wet conditions.

In an attempt to correlate neat resin properties with composite properties, neat resin moldings, Celion 3K-70P fabric composites and unidirectional Celion-12000 composites were prepared from several different formulations. The fracture energy of the neat resin moldings were low whereas the Gardner type impact of Celion 3K-70P composites of certain formulations indicated good impact resistance, suggesting that neat resin properties do not correlate with composite properties.

In one all-epoxy formulation, various loading levels and various molecular weights of polycarbonate, additive effect of CTBN at various loading levels with polycarbonate, effect of other thermoplastics as toughening agents, and various loading levels of Cab-o-sil were investigated. This study indicated that the maximum compatibility level for polycarbonates in this formulation was six parts by weight. Higher levels of polycarbonate improved the impact resistance and hot/wet composite properties but lowered prepreg tack and room temperature composite properties. Different molecular weight levels of polycarbonate failed to exert a definitive influence on impact resistance or composite properties. As the loading level of Cab-o-sil was increased from 2.5 to 8.5 parts by weight, the composite properties (impact resistance and short beam shear strength) generally decreased.

Less effort was placed on the epoxy/bismaleimide system than the all-epoxy system. Formulations were prepared with good Gardner type impact resistance and respectable composite properties. In general, the formulation work with the epoxy/bismaleimide system was more difficult than the all-epoxy system due to compatibility problems and higher cure temperatures. A basic study was conducted on a bismaleimide/epoxy formulation using Fourier transform infrared spectroscopy to investigate the cure chemistry. Several important

conclusions evolved from this study such as the overall cure rate is proportional to the amount of amine present, the amine/epoxy reaction is three times as fast at 423K (302°F) as the amine/maleimide reaction and hydroxyl groups do not add to the maleimide.

Although much useful fundamental information was generated during this contractual effort, a new heterogeneous laminating resin with significantly better impact resistance (damage tolerance) and performance otherwise equivalent to conventional (350°F) curing epoxy matrix systems was not developed.

The most significant conclusion established was that the toughness and impact resistance of matrix resin systems could be improved by the addition of certain elastomers and thermoplastics, but at a considerable sacrifice in other general mechanical properties.

SECTION 1

INTRODUCTION

This report summarizes the effort conducted during a 34.5 month contract to develop a heterogeneous laminating resin system with properties superior to state-of-the-art 450K curing epoxy systems for use as a matrix resin primarily with carbon/graphite reinforcement. Although conventional 450K curing epoxy systems (e.g. Narmco's 5208, Hexcel's F-263, Hercules' 3502, Fiberite's 934, etc.) find use in secondary composite structures on commercial airplanes, more extensive use of composite structures may be forthcoming if the composites had improved performance, particularly better damage tolerance. The use of structural composites in commercial aircraft in place of metal has been identified as a viable means of reducing the weight and thereby increasing the fuel efficiency.

This contract was initiated in September 1981 at a time when matrix materials such as conventional 450K curing epoxy systems were the best composite matrices available and new, more damage tolerant resin matrices had not yet been introduced into the marketplace. It was recognized that a higher strain carbon/graphite fiber was also needed to attain the improvement in damage resistance requested by the aerospace industry. Thus, high strain fibers and compliant matrix resins were both thought to be needed to provide high impact resistance in composites. The matrix resin must accommodate the increased fiber strain to meet impact resistance requirements and still provide efficient translation of fiber properties in composites to provide the strength requirements.

The work described herein concerns the formulation and evaluation of epoxy and epoxy/bismaleimide matrix systems. Various parameters were investigated in different formulations to determine the effect of formulation changes on properties.

SECTION 2

OBJECTIVE

The primary objective was to generate fundamental information on the effect of formulation changes during the development of a heterogeneous laminating resin having significantly improved impact resistance (damage tolerance) and equivalent performance in all other areas to the conventional 450K curing epoxy matrix system. The improved heterogeneous laminating resin system should also have improved processibility (shorter cure time, more forgiving cure cycle and longer prepreg shelf life) over 450K curing epoxy systems. The overall targets for the new laminating resin are contained in the following listing.

- Superior impact resistance - Impact resistance significantly better than conventional 450K curing epoxy systems as measured by a modified Gardner impact on woven graphite composites.
- Mechanical performance - Equivalent to or better than current 450K curing epoxy matrices (e.g. Narmco 5208).
- Simplified cure cycle - Straight up (no-dwell) cure cycle at 450K under 0.34 MPa (50 psi) using net resin prepreg with low flow requiring edge bleed only.
- Acceptable prepreg properties - Hot melt coatability with acceptable drape, tack, fiber collimation etc., and minimum out time of three weeks.

SECTION 3

DISCUSSION AND RESULTS

3.1 Resin Development Approaches

3.1.1 "All Epoxy" System

Two separate but interrelated approaches were studied. One involved formulation work with "all epoxy" systems. Various types of epoxies (see glossary in appendix) such as glycidyl ethers, glycidyl amines, epoxidized novolacs, bisphenol epoxies and toughened epoxies were used as the basic resin. Curing agents included 4,4'-diaminodiphenylsulfone (DDS), other standard aromatic amines, and a toughened aromatic amine. An accelerator (mixed substituted imidazoles, Resicure #4) was used in some formulations. The following two basic types of toughening agents were used.

- 1) Heterogeneous additives, as exemplified by carboxy terminated butadiene acrylonitrile (CTBN) technology which incorporates a precipitated dispersed second phase in the continuous primary resin phase.
- 2) Homogeneous additives which are soluble in the cured matrix network. Toughening agents (heterogeneous and homogeneous) included were moderately short chain saturated polyesters of various functionalities (degree or type), CTBN/epoxy prereacts, long chain polyethers and high molecular weight non-functional polymers (e.g. acrylonitrile butadiene styrene polymer (ABS), polycarbonate and polysulfone).

3.1.2 Epoxy/Bismaleimide Systems

A second approach has been to formulate with epoxy/bismaleimide systems. The major bismaleimide resin used was Kerimid 353, although Bis-maleimide-S and Bismaleimide-M were also given a cursory evaluation. The epoxy resins and curing agents have included the same materials as noted in the "all epoxy" part of the program. Preliminary work was required to define the chemistry of the simpler epoxy/bismaleimide/DDS combinations. Therefore, a systematically varied series of combinations of Bismaleimide-S/DER 331/DDS was prepared. The reaction paths and relative reaction rates were established by infrared analysis.

3.2 Screening Techniques

A rapid and reliable screening technique was needed for sensitive and accurate resin development efforts throughout this program. Narmco has developed in-house procedures for prepreg and laminate fabrication which have served well in formulation efforts over the years. Customarily Celion 3K-70P fabric is solution coated and dried to a low (0.5%) volatile content. A small 15.2 cm x 15.2 cm x 6 ply (6" x 6" x 6 ply) laminate is fabricated for Gardner impact screening tests. A set of criteria for damaged area measurements

(at 10, 20, 30, and 40 in.-lbs.) was previously developed at Narmco which shows a good correlation to the more sophisticated impact tests. The Gardner impact test (damaged area function) describes in somewhat quantitative terms the extent of damage suffered by the 6 ply laminate when impacted at 10, 20, and 40 in.-lbs. levels. This represents loadings up to 408.2 Kg-M/M (900 in.-lbs./in.) of thickness for the 1.1 cm (0.45 in.) thick laminates. The reported number (a weighted summation) is computed by an in-house developed equation which normalizes thickness and reduces data scatter by least square line fits. The number represents "impact sensitivity", where the smaller the reported number, the less damage is suffered upon impact. These results are inversely related to instrumented impact values where a larger number describes a tougher, more damage resistant system.

A second 10.2 cm x 15.2 cm x 12 ply (4" x 6" x 12 ply) was prepared for short beam shear (SBS) measurements. Candidate systems are routinely screened for room temperature, 366K (200°F) and 405K (270°F) SBS strength before and after 40 hr. water boil. This latter exposure seems to generally be more rigorous than the longer duration high humidity exposure at lower temperatures. The 40 hour water boil is at least as rigorous as long term exposures of up to 17 days at 315K (180°F) and 95 + % R.H. Saturation limits are generally experienced before the end of the exposure duration.

3.3 "All Epoxy" System Studies

Initial epoxy formulations were prepared utilizing hydroxy terminated saturated ester prepolymers, CTBN/epoxy prereacts, long chain polyethers and selected thermoplastics (ABS and polycarbonate) as toughening agents. A typical experimental procedure for the incorporation of such materials into epoxy systems is given in Appendix A. These systems were solution coated on woven Celion 3K-70P graphite fabric. Laminates were prepared for SBS and Gardner-type impact testing. The formulations and screening results are listed in Table 1. These results describe a wide range in both toughness (impact sensitivity) and SBS strengths, hot/wet in particular. Results from Narmco's 5208 and 5240 resin systems are included for comparison.

The brittle nature of Narmco 5208, evidenced by the 3300 impact damage area function, is not a significant drawback in the many applications where it is used. Narmco 5240 shows improved toughness, but obviously does not meet the high temperature performance profile of 5208. However, 5240, a relatively new resin system, was formulated with a third set of criteria in mind. In addition to improved impact damage resistance with a moderate use temperature capability, 5240/3K-70P must exhibit controlled flow during processing whereby a blemish-free surface results from lay-up and cure on a polished metal tool. This is obtained through careful balance of the matrix resin behavior during cure.

Table 1
"All Epoxy" Systems

Formulation No.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>5240</u>	<u>5208</u>
<u>Epoxies</u>											
DEN 439	11	11	11	11	11	11	11	11	11		
RCI 98-180	4	4	4	4	4	4	4	4	4		
MY 720	50	50	50	50	50	50	50	50	50		
<u>Hardener</u>											
DDS	21	21	21	21	21	21	21	21	21		
<u>Catalyst</u>											
Resicure #4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3			
<u>Filler</u>											
Cab-o-sil	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5		
<u>Toughening Agents</u>											
Hydroxyl Containing Polyether (high mol. wt.)	5		5								
Hydroxyl Containing Polyether (low mol. wt.)	8	10									
Polycarbonate				4							
ARS (K-2945)					6						
CTBN (I) ¹						6					
CTBN (II) ²							6				
<u>Short Beam Shear Strength, MPa^{3,4}</u>											
296K (73°F) (dry)	91.7	73.1	88.9	83.4	88.9	82.7	84.1	80.0	70.3	86.2	94.4
366K (199°F) (dry)	70.3	53.1	66.2	70.3	65.5	64.1	62.7	67.6	67.6	64.1	73.8
405K (270°F) (dry)	46.9	42.7	47.6	58.6	50.3	50.3	53.1	55.8	51.7	48.2	66.2
296K (wet) ⁵	68.9	67.6	77.9	66.9	73.1	73.1	69.6	66.2	71.0	75.8	83.4
366K (wet)	45.5	37.9	46.2	53.1	44.1	46.9	44.1	49.6	57.9	37.2	62.0
405K (wet)	18.6(P) ⁶	24.8(P)	25.5(P)	32.4(P)	26.2(P)	26.2(P)	24.8(P)	29.0(P)	42.7	P	51.7
<u>Gardner Type Impact Evaluation⁷</u>											
	415	600	1300	303	586	412	782	472	1964	677	3300

1. CTBN (I) = CTBN 1300 prereacted with an epoxy novolac

2. CTBN (II) = CTBN 1300 prereacted with MY 720

3. Cure: 0.31 MPa (45 psi), 2 hr. @ 450K (350°F), Celion 3K-70P graphite fabric

4. To convert MPa to psi, multiply by 144.9

5. Wet: 40 hr. water boil

6. P = soft, permanent deformation in specimen

7. Damaged area function, relative numbers

The "best" system in the initial studies (Table 1) is designated Formulation 4, which employs a Lexan (polycarbonate) as the toughening agent. The impact sensitivity over 5208 has been reduced by about an order of magnitude under the conditions of the test. The hot/wet SBS strengths at 366K (200°F), while lower than the 5208 values, are certainly adequate values. This homogeneous material resulted in prepreg with marginally light tack and drape, but good fiber wet-out impregnation. A surprising result was obtained with Formulation 8 (Table 1) with no toughening modifier. Hot/wet strengths were only slightly lower than Formulation 4 while the impact sensitivity was even less than 5240.

In the research, some of the tough epoxy materials are relatively transparent in appearance and do not show the opaqueness and whitening effect (when strained) that rubber toughened epoxy adhesives show. It is felt that it may be possible to develop useful toughened systems without having discreet "rubber" particles dispersed in a continuous phase.

Neat resin specimens and composites specimens were prepared from Formulations 4, 5, 8, and 9 in Table 1 and an adhesive system, Narmco's 117M (a rubber toughened epoxy). The highly loaded 117M is a very tough material with outstanding strain capability in metal-to-metal bonds. This material was selected to observe its performance in selected tests and compare it with the other formulations.

Unidirectional prepregs were prepared at $34 \pm 2\%$ resin content on $150 \pm \text{g/m}^2$ Celion 12000 fiber. Prepreg was also prepared using 3K-70P fabric. Neat resin moldings as well as composites were cured through 2 hr. at 450K. The results are presented in Tables 2, 3, and 4. The SBS strength for the 3K-70P composites in Table 2 compared favorably with those reported for the same formulations in Table 1. The Gardner type impact test however showed a small difference for Formulation 4, essentially the same values for Formulations 5 and 9, and significant difference for Formulation 8. The glass transition temperatures (T_g) are also reported in Table 2. Neat resin properties are reported in Table 3. Formulation 4 (contains polycarbonate) and 8 (no polycarbonate) gave similar mechanical properties including fracture toughness. Although the Gardner-type impact test (Table 2) gave a relatively low value for Formulation 4 suggesting good impact resistance, the fracture energy for neat resin moldings of Formulation 4 (Table 3) was low. The Gardner type impact for 117M was also low (Table 2) while the fracture energy (Table 3) was high. This study suggests that it may be improper to predict the impact performance of a resin in a composite based upon neat resin properties.

Unidirectional Celion 12000 composite properties are reported in Table 4. The compression strength of the composite from Formulation 9 was the highest of the four formulations. Formulation 9 also has the highest neat resin tensile modulus (Table 3). The SBS strengths of Formulation 9 composites were also relatively high. The composite properties in Table 4 do not correlate with that expected based upon the neat resin properties in Table 3. Specifically, Formulation 9 has the lowest fracture toughness in a neat casting and yet woven and unidirectional composite properties are relatively good, especially short beam shear.

Table 2
Properties of 3K-70P Woven Fabric Composites

<u>Formulation No.</u>	<u>4</u>	<u>5</u>	<u>8</u>	<u>9</u>	<u>117M</u>
Short Beam Shear Strength, MPa *					
296K (dry)	76.7	77.2	82.7	70.2	-
366K (dry)	68.8	59.2	68.0	67.6	-
405K (dry)	58.7	43.3	48.3	51.7	-
296K (wet)	76.5	68.9	72.9	71.0	-
366K (wet)	54.8	44.4	51.7	57.7	-
405K (wet)	35.1	28.7	31.4	42.4	-
Gardner Type Impact Evaluation	419	575	915	1960	277
Glass Transition Temp., K(°F)	475(396)	470(387)	501(442)	503(446)	379(223)
*To convert MPa to psi, multiply by 144.9					

Table 3
Neat Resin Properties*

<u>Formulation No.</u>	<u>4</u>	<u>8</u>	<u>9</u>	<u>117M</u>
Clarity of Molding	Clear	Opaque	Clear	Clear
Tensile Strength, MPa	58.3	66.6	66.3	56.1
Tensile Modulus, GPa**	357.1	302.6	596.7	225.4
Elongation, %	2.2	3.2	1.0	7.1
Fracture Toughness (G_{IC}), J/m ²	190	185	85	3400 onset 5700 (steady crack growth @ 0.018 cm/sec.)

* Average of 4 specimens tested by NASA Langley
 **To convert GPa to psi, multiply by 144.9×10^3

Table 4
Unidirectional Celion 12K Composite Properties*

<u>Formulation No.</u>	<u>4</u>	<u>5</u>	<u>8</u>	<u>9</u>
296K Compressive Strength, MPa	1348	1362	1417	1682
296K Compressive Modulus, GPa	90.6	97.2	111.7	111.0
296K Tensile Strength, MPa	1923	1841	1709	1806
296K Tensile Modulus, GPa	126.8	119.3	122.0	122.0
296K Tensile Elongation, %	1.4	1.4	1.3	1.4
SBS Strength, MPa				
296K (dry)	101.8	88.0	96.5	102.7
366K (dry)	78.1	62.5	69.8	79.8

* Average of 4 specimens tested by NASA Langley

In continuing the effort to improve the toughness of our "all epoxy" systems, a study with Ciba Geigy's LSU-931 hardener was initiated. This curing agent is described as a "modified DDS" and is marketed as a material which results in tougher cured epoxies than DDS cured systems. The mechanical properties of epoxies using the LSU-931 hardener evidently show only nominal sacrifice in high temperature performance. Two other advantages are:

- 1) The melting point of LSU-931 is lower than DDS which facilitates mixing.
- 2) The amine equivalent weight is about twice the value of DDS.

A simple 50/50 DDS/931 mixture in a toughened MY-720/Epiclon 830 epoxy matrix (Formulation 10, Table 5) was evaluated and exhibited inadequate hot/wet SBS performance but slightly improved impact resistance. Epiclon 830 is essentially the diglycidyl ether of bisphenol F (from formaldehyde and phenol) and is useful as a low viscosity difunctional diluent.

Two modifications (Formulations 11 and 12, Table 5) were then made in attempts to improve the hot/wet properties; both using Ancamine 1482 (a mixture of m-phenylenediamine and 4,4'-methylenedianiline). The SBS strengths and impact damage resistance on Celion 3K-70P graphite fabric are presented in Table 5. The hot/wet properties at 366K (for Formulations 11 and 12) were improved slightly over Formulation 10 but the impact resistance did not show a substantial improvement. The hot/wet values at 405K were in the same range as Formulation 10.

The stoichiometry values (amine/epoxy) coincidentally show a direct correlation with the damage area value generated during impact testing (a small number indicating a more damage resistant system). The impact resistance results are respectable. The hot/wet SBS values show an opposite relationship with stoichiometry. These two relationships imply that a softer more compliant material is obtained with lower amine/epoxy ratio, at least in this apparently sensitive low stoichiometry region.

In view of these results, further work with the LSU-931 was conducted. The simple MY-720/931 system (13) in Table 5 did not appear promising. Elevated temperature SBS strengths were inadequate and the impact sensitivity was surprisingly high. Modifications with Epiclon 830 (14, Table 5) to improve drape and tack characteristics and incorporation of polycarbonate to improve the impact properties were only partly effective. Impact sensitivity was substantially improved but at a sacrifice in strength properties.

Partial replacement of the LSU-931 with Ancamine 1482 in a slightly modified equivalent system improved the hot (dry and wet) strength properties over the original formulation, but at a cost of returning to the relatively high level of impact sensitivity (15, Table 5).

Table 5
"All Epoxy" Systems

<u>Formulation No.</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>
<u>Epoxyes</u>						
MY-720	61.5	63.0	40.0	63.7	59.7	65.7
Epiclon 830	5	5	6		5	4
DER 669			4			
DEN 439			18			
<u>Hardeners</u>						
DDS	15	9				
LSU 931	15	18	23	36	35	27
Ancamine 1482		3	5			3
<u>Catalyst</u>						
Resicure #4	0.3		0.3	0.3	0.3	0.3
<u>Filler</u>						
Cab-o-sil	3.5	3.5	3.5	3.5	3.5	3.5
<u>Toughening Agent</u>						
Polycarbonate	2.0	2.0	4.0		3.5	3.5
<u>Short Beam Shear Strength,*</u>						
MPa						
296K (dry)	84	79.3	64.3	71.3	70.7	86.3
366K (dry)	66.9	66.9	58.6	51.0	43.3	63.2
405K (dry)	49.6	51.0	40.0	30.4	15.2	36.0
296K (wet)	72.4	64.8	63.4	56.9	52.8	72.1
366K (wet)	39.3	48.3	48.4	29.4	24.2	38.1
405K (wet)	P**	25.5(P)	25.8(P)	P	P	16.5(P)
<u>Gardner Type Impact</u>						
Resistance	149	182	164	949	265	922

* Cure through 2 hrs. at 450K

**P = soft breaks, specimen above permanent deformation

Three more systems (Formulations 16, 17, 18, Table 6) were formulated to further evaluate LSU-931 hardener. XU-276 (Ciba Geigy), which is described as a "toughened" epoxy resin was also included in these systems. Formulas 16, 17, and 18 (Table 6) utilize Ciba Geigy's 0510 as a replacement for Epiclon 830 (both being low viscosity resins) in an effort to increase the hot/wet strengths while retaining high impact resistance. Formulations 17 and 18 (Table 6) utilize the XU-276 epoxy to determine its possible utility as a "tough" matrix resin. Formulations 16, 17, and 18 (Table 6) exhibited inadequate elevated temperature properties and unexpectedly high impact sensitivity.

More polycarbonate formulations were prepared as presented in Table 7. The new "toughened" epoxy, XU-276, was evaluated as the base resin in Formulations 18 and 19. The low SBS strength at 405K and the high impact resistant values were disappointing. In addition, the prepreg from Formulations 18, 19, and 20 did not exhibit adequate tack to be of practical use. Other formulations were prepared in an attempt to maximize the impact resistance while retaining high SBS strength and tack and drape in the prepreg. Formulations 18-24 in Table 7 and 25-27 in Table 8 failed to exhibit the overall combination of properties as obtained for Formulation 4 in Table 1.

Since one of the early formulations (4, Table 1) showed the best overall combination of properties including prepreg tack and drape, it was decided with the mutual consent of NASA Langley to focus the remaining contractual effort on this system. The basic formulation was held constant, [the same as Formulation 4 (Table 1)] and the following parameters were varied:

1. Various loading levels of polycarbonate
2. Various molecular weight levels of polycarbonate
3. Additive effect of CTBN at various loading levels with polycarbonate
4. Other thermoplastics as toughening agents
5. Various loading levels of cab-o-sil

The effect of various loading levels of polycarbonate (Lexan) upon SBS strength, impact resistance and water pickup is presented in Table 9. Incorporation of Lexan is difficult. It was accomplished by adding a dilute solution of Lexan (10-15% in methylene chloride) to a diluted warm mixture of the rest of the formulation under vigorous stirring. Solvent was then vacuum extracted from the resin mix. Apparently six parts by weight (pbw) appears to be the limit of compatibility. Attempts to go beyond this resulted in precipitation, presumably of excess Lexan. Revising the basic formulation to increase compatibility would be feasible but would change the base resin formulation. Additionally, at six pbw, the resultant prepreg was extremely

Table 6
"All Epoxy" Systems

<u>Formulation No.</u>	<u>16</u>	<u>17</u>	<u>18</u>
<u>Epoxies</u>			
MY 720	50		
0510	5	5	5
DER 669	3	3	2
DEN 439	8.7	5.0	5.0
XU 276		57.0	67.7
<u>Hardeners</u>			
DDS			16
LSU 931	24	22.5	
Ancamine 1482	5.0	3.2	
<u>Catalyst</u>			
Resicure #4	0.3	0.3	0.3
<u>Filler</u>			
Cab-o-sil	3.5	3.5	3.5
<u>Toughening Agent</u>			
Polycarbonate	4	4	4
<u>Short Beam Shear</u>			
<u>Strength, MPa *</u>			
296K (dry)	76.5	67.4	71.7
366K (dry)	44.8	59.8	51.7
405K (dry)	P	38.6	P
<u>Gardner Type Impact</u>			
<u>Resistance</u>	1310	1084	784

*Cure through 2 hrs. @ 450K

Table 7
"All Epoxy" Systems

<u>Formulation No.</u>	<u>18</u> (X126-14-1)	<u>19</u> (X126-14-2)	<u>20</u> (X126-14-3)	<u>21</u> (X126-23-1)	<u>22</u> (X126-23-2)	<u>23</u> (X126-23-3)	<u>24</u> (X126-23-4)
<u>Epoxies</u>							
MY 720	-	-	50.0	51.0	51.0	51.0	51.0
ERL 0510	5.0	5.0	5.0	5.0	5.0	5.0	5.0
DEN 439	5.0	5.0	8.7	7.0	7.0	7.0	7.0
RCI 98-180	-	-	-	3.0	3.0	3.0	3.0
XU 276	67.7	57.0	-	-	-	-	-
<u>Hardeners</u>							
LSU 931	-	22.5	24.0	23.0	23.0	23.0	23.0
XU 205	-	-	-	7.0	7.0	7.0	7.0
DDS	16.0	-	-	-	-	-	-
Anchor 1482	-	3.2	5.0	-	-	-	-
<u>Catalyst</u>							
Resicure #4	0.3	0.3	0.3	0.3	0.3	0.3	0.3
<u>Filler</u>							
N Cab-o-sil M-5	3.5	3.5	3.5	3.0	3.0	3.0	3.0
<u>Toughening Agent</u>							
Lexan	4.0	4.0	4.0	-	4.0	4.0	4.0
DER 669	2.0	3.0	3.0	-	-	3.0	3.0
Photomer 4127	-	-	-	-	-	-	1.0
<u>Stoichiometry</u>							
Eqs. NH/Epoxy	0.66	0.77	0.64	0.59	0.59	0.59	0.59
<u>Gel Time @ 436K(325°F)</u>	-	-	-	12'00"	12'40"	12'32"	13'04"
<u>SBS Strength, MPa*</u>							
296K (dry)	72.0	76.3	66.4	76.2	70.3	83.3	81.1 (82.7)
366K (dry)	51.4	44.8	55.4	62.7	62.9	65.1	64.6 (67.6)
405K (dry)	19.4	9.5	43.8	44.5	42.7	46.1	48.9 (55.8)
296K (wet)	-	-	68.7	69.4	72.0	73.1	72.7 (72.9)
366K (wet)	-	-	46.9	44.6	43.8	47.6	46.4 (52.4)
405K (wet)	-	-	27.0	21.9	19.6	20.0	17.4 (38.4)
<u>Impact Resistance</u>	784	1084	144	1560	655 (624)	379 (562)	632 (524)

*Cure through 2 hrs. @ 450K

NOTE: Values in parentheses obtained on post-cured samples (4 hrs. @ 400°F)

Table 8
"All Epoxy" Systems

<u>Formulation No.</u>	<u>25</u> (X-126-26-1)	<u>26</u> (X-126-26-2)	<u>27</u> (X-126-27-1)
<u>Epoxies</u>			
MY 720	53	53	51
ERL 0510	5	5	5
DEN 439	5	-	4
RCI-98-180	-	-	3
<u>Hardeners</u>			
LSU 931	23	23	24
XU 205	7	7	7
<u>Catalyst</u>			
Resicure #4	0.3	0.3	0.3
<u>Filler</u>			
Cab-o-sil M-5	3	3	3
<u>Toughening Agents</u>			
Lexan	4	4	3
DER 669	3	3	3
SR 5217A	-	5	-
<u>Gel Time @ 436K</u>	11'20"	10'10"	12'50"
<u>Prepreg Tack</u>	Dry	Very light	Light
<u>Impact Resistance*</u>	758 (733)	1118 (844)	-

*Cure through 2 hrs. @ 450K

NOTE: Values in parentheses obtained on post-cured samples [4 hrs. @ 477K (400°F)]

Table 9
Effect of Loading Levels of Lexan

<u>Formulation No.</u>	<u>28</u> (X-126-30-0)	<u>29</u> (X-126-30-2)	<u>30</u> (X-126-30-4)	<u>31</u> (X-126-30-6)
<u>Epoxies</u>				
DEN 439	11	11	11	11
RCI 98-180	4	4	4	4
Ciba MY 720	50	50	50	50
<u>Hardener</u>				
DDS	21	21	21	21
<u>Catalyst</u>				
Resicure #4	0.3	0.3	0.3	0.3
<u>Filler</u>				
Cab-o-sil	4.5	4.5	4.5	4.5
<u>Toughening Agent</u>				
	0	2	4	6
47 <u>Short Beam Shear, MPa*</u>				
296K (dry)	88.9	86.2	71.7	67.6
366K (dry)	69.6	74.5	70.3	68.2
405K (dry)	50.3	64.1	60.0	60.0
296K (wet)	70.3	72.4	71.7	68.3
366K (wet)	36.5	52.4	53.1	53.1
405K (wet)	19.3P**	33.8	33.1	39.3
<u>Impact Resistance</u>	564	689	390	356
<u>%Water Gain</u>	1.9	1.6	1.4	1.6

* Cure through 2 hrs. @ 430K

**Plastic

dry (extremely light tack) and therefore would be difficult to use. It should be noted that the base resin (Formulation 30) shows relatively good toughening behavior (relative to 5208, Table 1), presumably due to the less brittle epoxy novolacs.

Data in Table 9 indicate an effect of improved SBS strengths at higher temperatures (both wet and dry) by inclusion of Lexan. This is surprising and may be due to Lexan acting as an IPN agent at higher temperatures overcoming the expected plasticizing effect. The optimum impact resistance is at four pbw (Formulation 30). Addition of another two pbw (Formulation 31) does not improve impact resistance appreciably and results in a poorer prepreg.

Formulation 28 (Table 9) is the same as Formulation 8 (Table 1) while Formulation 30 is the same as Formulation 4 (Table 1). There is some variation in SBS strengths between Formulations 8 and 28 especially at RT (28 higher) and wet at 366K (8 higher). The SBS strengths for Formulations 4 and 30 are similar except that Formulation 4 had a higher dry 296K value. Impact resistances were comparable and within experimental reproducibility.

Lexan (120, 141, 101 and 131) of four different molecular weights as suggested by viscosity measurements at 573K (572°F) were incorporated within the basic resin formulation as shown in Table 10. Past work has used Lexan 141 only. Although the lower molecular weight Lexan 120 (Formulation 32) gave the best impact resistance, the higher molecular Lexan 131 (Formulation 35) gave the best SBS strengths. Formulation 34 is identical to Formulation 4 (Table 1) and 30 (Table 9). The Gardner type impact test has given values of 303, 390 and 532 for Formulations 4, 30 and 33 respectively. Little scatter in impact resistance within specimens from the same composite has been observed in past work at Narmco. The reason for the differences in the impact values, especially from 303 to 532, is unknown. Formulation 33 provided a SBS strength wet at 405K of 45.5 MPa, much higher than that obtained for Formulation 4 (32.4 MPa) or 30 (33.1 MPa).

The effect of incorporating rubber (Hycar 1472) within the basic formulation with Lexan 131 (highest molecular weight polycarbonate from the study in Table 10) is shown in Table 11. Hycar 1472 is a copolymer of butadiene and acrylonitrile (27% acrylonitrile content) with carboxy groups and a molecular weight of ~10,000. As expected, significant toughening or improved impact resistance occurred but at the expense of lowering the SBS strengths. Because of this compromise, it does not appear beneficial to incorporate Hycar 1472 into the formulation.

The effect of various loading levels of Cab-o-sil was evaluated and the results are presented in Table 12. SBS strengths under dry conditions were higher for the lower loading levels of Cab-o-sil and under wet conditions, higher for the highest loading level of Cab-o-sil. A trend towards less impact resistance was observed with increased levels of Cab-o-sil. The role of the Cab-o-sil is to control flow and it appears that the lowest Cab-o-sil loading consistent with proper flow and SBS strength is best.

Table 10
Effect of Lexan with Different Molecular Weights

	Formulation No.			
	<u>32</u> (X-126-31-1)	<u>33</u> (X-126-31-2)	<u>34</u> (X-126-31-3)	<u>35</u> (X-126-31-4)
<u>Epoxies</u>				
DEN 439	11	11	11	11
RCI 98-180	4	4	4	4
Ciba MY-720	50	50	50	50
<u>Hardener</u>				
DDS	21	21	21	21
<u>Catalyst</u>				
Resicure #4	0.3	0.3	0.3	0.3
<u>Filler</u>				
Cab-o-sil	4.5	4.5	4.5	4.5
<u>*Toughening Agents</u>				
[viscosity @ 573K (572°F)				
cps]				
Lexan 120 (1600-2400)	4.0	-	-	-
Lexan 141 (2400-3400)	-	4.0	-	-
Lexan 101 (4400-6000)	-	-	4.0	-
Lexan 131 (8500-11500)	-	-	-	4.0
<u>Short Beam Shear (MPa)**</u>				
296K (dry)	75.1	74.5	67.6	81.3
366K (dry)	68.3	73.1	62.0	73.1
405K (dry)	61.4	66.9	57.2	66.9
296K (wet)	71.7	74.5	68.3	77.6
366K (wet)	55.2	59.3	53.8	60.0
405K (wet)	37.2	45.5	40.7	48.9
<u>Impact Resistance</u>	345	532	476	496

* Listed in order of increasing MW

**Cure through 2 hrs. @ 450K

Table 11
Effect of Incorporating Hycar 1472

<u>Formulation No.</u>	<u>36</u> (X-126-31-4)	<u>37</u> (X-137-6-1)	<u>38</u> (X-137-6-2)	<u>39</u> (X-137-6-3)
<u>Epoxies</u>				
DEN 439	11	11	11	11
RCI 98-180	4	4	4	4
Ciba MY-720	50	50	50	50
<u>Hardener</u>				
DDS	21	21	21	21
<u>Catalyst</u>				
Resicure #4	0.3	0.3	0.3	0.3
<u>Filler</u>				
Cab-o-sil	4.5	4.5	4.5	4.5
<u>Toughening Agents</u>				
Lexan 131 (Polycarbonate)	4.0	4.0	4.0	4.0
Hycar 1472 (Nitrile Rubber)	-	0.5	1.0	2.0
<u>Short Beam Shear (MPa)*</u>				
296K (dry)	81.3	77.9	68.9	57.9
366K (dry)	73.1	71.0	64.1	59.5
405K (dry)	66.9	58.6	56.5	50.3
296K (wet)	77.2	74.5	69.6	64.1
366K (wet)	60.0	55.8	52.2	52.4
405K (wet)	48.9	36.5	39.3	38.6
<u>Impact Resistance</u>	496	440	245	178

*Cure through 2 hrs. @ 450K

Table 12
Effect of Cab-o-sil Loading Level

<u>Formulation No.</u>	<u>40</u> (X-137-10-1)	<u>41</u> (X-137-10-2)	<u>42</u> (X-137-10-3)	<u>43</u> (X-137-10-4)
<u>Epoxies</u>				
DEN 439	11	11	11	11
RCI 98-180	4	4	4	4
Ciba MY-720	50	50	50	50
<u>Hardener</u>				
DDS	21	21	21	21
<u>Catalyst</u>				
Resicure #4	0.3	0.3	0.3	0.3
<u>Filler</u>				
Cab-o-sil	2.5	4.5	6.5	8.5
<u>Toughening Agent</u>				
Lexan 131 (Polycarbonate)	4.0	4.0	4.0	4.0
<u>Short Beam Shear (MPa)*</u>				
296K (dry)	73.1	72.4	63.4	59.3
366K (dry)	71.0	60.3	64.1	60.7
405K (dry)	62.7	66.2	66.9	60.7
296K (wet)	76.5	74.5	67.6	63.4
366K (wet)	53.8	55.2	55.8	48.3
405K (wet)	26.2	26.9	34.5	37.2
<u>Impact Resistance</u>	418	555	684	599

*Cure through 2 hrs. @ 450K

Two other thermoplastics, polyethersulfone and polysulfone, were evaluated as toughening agents in place of Lexan. The thermoplastics were incorporated within the formulation using methylene chloride as previously described for Lexan. The results are shown in Table 13. The impact resistance for the polyethersulfone (Formulation 44) and polysulfone (Formulation 45) systems are not as good as for the Lexan formulation (46). The SBS strengths were mixed with the Lexan formulation generally providing better overall values.

3.4 Bismaleimide/Epoxy Systems

The interest in bismaleimide/epoxy systems was prompted by a concern that the "all epoxy" systems may not provide an attractive combination of impact resistance and hot/wet composite properties because of trade-offs encountered in toughening epoxy systems. The higher temperature capability of bismaleimides and the demonstrated co-curability with amine cured epoxy resins was attractive. These higher Tg materials, which would offer more room for toughening, were expected to result in superior performance materials.

A typical experimental procedure for the incorporation of toughening agents into bismaleimide/epoxy systems is given in Appendix B.

The first two formulations (47 and 48) in Table 14 reflect an initial step toward a simple screening system which would allow estimation of the toughening brought about by selected additives. Although the impact resistance looks attractive, the mechanical performance was disappointingly low. Note that many of these early systems (47 and 48) were designed to lend themselves to prepregging processibility.

Table 14 also includes a second base formulation (49-56) using a higher proportion of epoxy and hardener which develops very good properties upon cure and seems to readily accept the various toughening additives. Cab-o-sil was required to control flow. These formulations had 60% of stoichiometric amine content. Cure is achieved through homopolymerization of the residual unsaturation of the maleimide groups and postcured unrestrained at 505K (450°F) for four hours.

Formulas 49, 50, 51 and 52 (Table 14) are interesting. Formula 49 contains no toughening additives, Formula 50 a heterogeneous thermoplastic additive (ABS) and Formulas 51 and 52 heterogeneous rubber additives (CTBN/epoxy prereacts). The impact resistance is similar for the 4 formulations. In addition, short beam shear strengths are also similar except the strength at 405K wet is higher for Formulation 49. It was surprising to observe the performance of Formulation 49 and especially its impact strength although it did not contain any toughening agent.

Table 13
Effect of Other Thermoplastic Toughening Agents

	<u>44</u> 130-80-1	<u>45</u> 130-80-2	<u>46</u> X-137-10-2
<u>Formulation No.</u>			
<u>Epoxies</u>			
DEN 439	11	11	11
RCI 98-180	4	4	4
MY-720	50	50	50
<u>Hardener</u>			
DDS	21	21	21
<u>Catalyst</u>			
Resicure #4	0.3	0.3	0.3
<u>Filler</u>			
Cab-o-sil	4.5	4.5	4.5
<u>Toughening Agents</u>			
Polyethersulfone (GR200P)	4.0		
Polysulfone (Udel P-1700)		4.0	
Lexan			4.0
<u>Short Beam Shear Strength (MPa)*</u>			
296K (dry)	71.7	61.4	72.4
366K (dry)	66.9	64.1	68.3
405K (dry)	54.5	55.2	66.1
296K (wet)	75.1	72.4	74.5
366K (wet)	50.3	53.1	55.2
405K (wet)	30.3	35.2	26.9
<u>Impact Resistance</u>	750	692	555

*Cure through 2 hrs. @ 450K

Table 14
Bismaleimide/Epoxy Systems

Formulation No.	<u>47</u>	<u>48</u>	<u>49</u>	<u>50</u>	<u>51</u>	<u>52</u>	<u>53</u>	<u>54</u>	<u>55</u>	<u>56</u>	<u>5208</u>	<u>5245C</u>
<u>Resin</u>												
Bismaleimide K-353	50	50	24	24	24	24	24	24	24	24	-	-
<u>Epoxyes</u>												
MY-720	30	30	-	-	-	-	-	-	-	-	-	-
Ciba 0510	-	-	45	45	45	45	45	45	45	55	-	-
XU-276	-	-	-	-	-	-	-	-	-	14	-	-
<u>Hardener</u>												
DDS	10	10	24	24	24	24	24	24	24	14	-	-
<u>Catalysts</u>												
Resicure #4	.3	.3	.3	.3	.3	.3	.3	.3	-	-	-	-
ETPI	-	-	-	-	-	-	-	-	.2	.3	-	-
<u>Filler</u>												
Cab-o-sil	-	-	4.5	4.5	4.5	4.5	4.5	4.5	2	2	-	-
<u>Toughening Agents</u>												
Hydroxyl Containing Polyether (High M.W.)	8	5	-	-	-	-	-	-	-	-	-	-
Hydroxyl Terminated Polyester (Low M.W.)	2	-	-	-	-	-	8	-	-	-	-	-
ABS	-	-	-	6	-	-	-	4	6	6	-	-
Polycarbonate	-	5	-	-	-	-	-	2	-	-	-	-
CTBN/Epoxy I*	-	-	-	-	6	-	-	-	-	-	-	-
CTBN/Epoxy II**	-	-	-	-	-	6	-	-	-	-	-	-
<u>SBS (MPa)</u>												
296K (Dry)	54.4	49.0	53.1	51.7	55.2	60.0	55.9	58.6	72.4	89.7	94.5	86.2
366K (Dry)	49.6	42.1	55.9	56.6	56.6	60.0	54.4	57.2	65.5	79.3	73.8	77.2
405K (Dry)	40.7	35.2	64.8	49.0	55.9	57.9	53.8	59.3	51.7	61.4	66.2	64.8
296K (Wet)***	46.2	61.4	58.6	62.1	60.0	57.2	59.3	64.8	65.5	93.8	83.5	82.8
366K (Wet)	35.2	31.8	55.2	46.2	47.6	51.0	46.2	53.8	47.6	62.1	62.1	69.7
405K (Wet)	25.5	20.0	47.6	31.8	37.9	35.9	31.0	36.6	32.4	39.3	51.7	59.3
Impact Resistance	261	305	738	706	832	679	622	641	678	790	3300	270

* CTBN 1300 prereacted with epoxy novolac.

** CTBN 1300 prereacted with MY-720.

***40 hr. water boil.

Cure: 45 psi fpr 2 hrs. at 450K (350°F)

Post Cure: 4 hrs. unrestrained at 505K (450°F)

As noted in Table 14, the impact resistance of the bismaleimide/epoxy systems is less than the "all epoxy" materials. The hot/wet properties, however, are better than the "all epoxy" systems. Formula 49, void of any toughening agent, gave the best overall properties in the initial studies.

As formulation work proceeded with the bismaleimide/epoxy/amine systems, fundamental research was performed to investigate the cure chemistry. Using a Nicolet Model 7199 Fourier transform infrared spectrophotometer, the following three formulations were studied.

- A. An uncatalyzed mixture of DER 331 (standard bisphenol-A based epoxy resin from Dow Chemical Company), Bismaleimide-S (essentially pure bismaleimide 4,4'-methylenedianiline from Mitsui Toatsu), and DDS in a 1/1/1 molar ratio, i.e. two equivalents of epoxy, two of maleimide, and four of N-H functionalities.
- B. A catalyzed (0.2% Benzyldimethylamine) version of A above.
- C. A 1/1/.05 molar ratio of the A mixture, i.e. 50% of the stoichiometric amount of NH_2 assuming reaction between amine (N-H) and both epoxy (ring opening) and unsaturation (Michael-type addition).

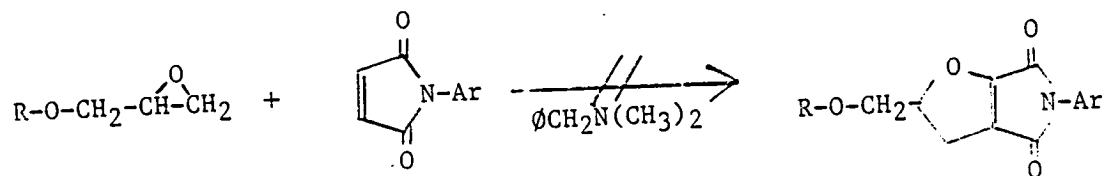
The formulations were coated onto sodium chloride plates and placed into a well regulated oven. Samples were removed after 20, 40, 60, and 90 minutes of cure at 423K (302°F). To complete the cure and establish a baseline reference for subsequent computer subtractions, the 90 minute sample was heated an additional 60 minutes each at 483K (410°F) and at 487K (417°F).

The aromatic ring absorption at 1513 cm^{-1} was selected as the reference peak in all measurements. The absorptions at 915 cm^{-1} for the epoxy ring, 1625 cm^{-1} for the maleimide unsaturation and the N-H stretch vibrations at 3471 cm^{-1} , 3377 cm^{-1} , and 3246 cm^{-1} were all monitored and changes quantified by subtraction and scale expansion techniques.

A reference spectrum of fully cured A formulation (the uncatalyzed 1/1/1 mixture) was taken after 90 minutes at 483K plus 60 minutes at 477K (397°F) plus one hour at 487K. This spectrum showed no residual amine, epoxy or unsaturation demonstrating complete utilization of cure functionality at this stoichiometry. The reference spectrum was then subtracted from the spectrum of the partially cured materials which were taken after 20, 40, 60, and 90 minutes at 423K respectively to yield the difference spectra of these and others.

Many infrared spectra were obtained and curves were drawn showing residual functionality under a variety of cure conditions (time and temperature). The conclusions reached from these studies are summarized as follows:

1. The overall rate at any time is proportional to the amount of -NH in the system.
2. Hydroxyl groups do not add to the maleimide unsaturation, whether catalyzed or not.
3. The reaction rate slows markedly after about 60 minutes, probably due to the Tg of the curing material reaching the cure temperature of 423K.
4. The -NH epoxy reaction is about three times as rapid (at 423K) as the addition of -NH across the double bond.
5. No residual functionality remains in the 1/1/1 (catalyzed or uncatalyzed) cases after the 423K post cure. This includes epoxy, unsaturation and -NH.
6. Some residual epoxy functionality is apparent in the 1/1/.05 (50% -NH stoichiometry) postcured material, implying homopolymerization of the maleimide at elevated temperature.
7. No evidence for homopolymerization of the epoxy to form a crosslinked polyether structure was found under these conditions.
8. No evidence for the reaction of epoxy with hydroxyl (in the presence of primary or secondary amine) was found.
9. Tertiary amine catalyzed cycloaddition of epoxy across the maleimide unsaturation does not appear to go.



10. A very weak absorption at approximately 1200 cm^{-1} has tentatively been assigned to secondary amine formation by reaction between DDS and epoxy groups.

Various other bismaleimide/epoxy systems were formulated as presented in Table 15 using a heterogeneous toughening route for Formulations 57, 58 and 59. SR-5217A is a product of DEN 411 (novolac epoxy resin) and a CTBN with triphenyl phosphine and 10301 is an 80/20 blend of diglycidyl ether of bisphenol A and a long chain polyether diamine. Relatively high impact strength is demonstrated by Formulations 57 and 58 but poor SBS strengths, especially at 405K. Formulation 59 containing a free radical curing vinyl ester based upon bisphenol A (Diacryl-101) showed better SBS strength at elevated temperature with only slightly less impact resistance. Formulations 60 and 61 gave less impact resistance than Formulation 59 but did have improved prepreg tack. The SBS strengths of Formulation 61 were good but further work with this formulation was not conducted due to the poor impact resistance.

Table 16 describes six formulations (62-67) designed to screen heterogeneous toughening. The rationale for these formulations is as follows:

62 - serves as a baseline.

63 - incorporates Dicap (Dicumyl peroxide) to establish the effects of earlier initiation of bismaleimide homopolymerization (less Michael-like addition of the aromatic amine across the residual double bond of the maleimide). An effect due to better adhesion brought about by maleimide-butadiene reaction may also be present.

64 - total replacement of the "latent" DDS with a more active aromatic amine mixture. (More Michael addition reaction probable.)

65 - increase total amine/epoxy plus BMI stoichiometry with incorporation of the polymer toughened epoxy (XU-276).

66 - tighten up the cured system by reduction of 661 and increasing the 830 content. The CTBN adduct level is similarly reduced. A less damage resistant material with better high temperature mechanicals was expected. Handling characteristics show improvement.

67 - offset comparison of XU-205 with Anchor 1482 (lower amine equivalent weight).

Unfortunately, none of the formulations provided a good combination of prepreg tack, SBS strength and impact resistance.

During the course of performing the studies of the bismaleimide/epoxy systems, it was observed that continued post-curing at 505K (450°F) resulted in a significant improvement in impact behavior. As shown in Figure 1, the reduction in impact damage is noticeable beyond the 4 hrs. used in the normal cure of the systems reported in the maleimide/epoxy data tables.

Table 15
Bismaleimide/Epoxy Systems

<u>Formulation No.</u>	<u>57</u> X-126-21-1	<u>58</u> X-126-21-2	<u>59</u> X-126-21-3	<u>60</u> X-126-25-1	<u>61</u> X-126-25-2
<u>Resins</u>					
Bismaleimide K-353	24	24	30	30	30
XU 205				10	10
Eponol B55-40	6	6	6		
Epiclon 830	30	35	6	10	10
DEN 438	5	6	5		
Diacryl 101			22	30	30
DER 661				10	10
<u>Hardeners</u>					
LSU 931	20	15	16.6		
Anchor 1482	5	4	4.4		
<u>Toughening Agents</u>					
SR-5217A	5	5	5		
10301	5	5	5		
<u>Catalysts</u>					
ETPPI			0.2	0.2	0.2
Dicumyl Peroxide			0.5		0.3
Ancamine 1222	1	1		0.4	
<u>Filler</u>					
Cab-o-sil M-5				3.0	3.0
<u>Gel Time @ 436K(325°F)</u>	3'50"	5'32"	2'50"	4'00"	4'03"
<u>Stoichiometry</u>	0.726	0.611	0.775	-	-
<u>Prepreg Tack</u>	-	-	dry	light	light
<u>Short Beam Shear Strength, MPa*</u>					
296K (dry)	66.2	70.2	67.6	55.1	80.0
366K (dry)	42.1	45.5	53.4	39.6	66.1
405K (dry)	17.2	21.4	40.7	26.2	46.3
296K (wet)	59.0	62.4	64.5	-	73.2
366K (wet)	P	P	39.2	-	48.8
405K (wet)	P	P	24.1	-	27.8
<u>Impact Resistance</u>	343	334	452	720	606

*Cure: 2 hr. @ 450K. Postcure: 4 hr. @ 491K(425°F).

Table 16
Bismaleimide/Epoxy Systems

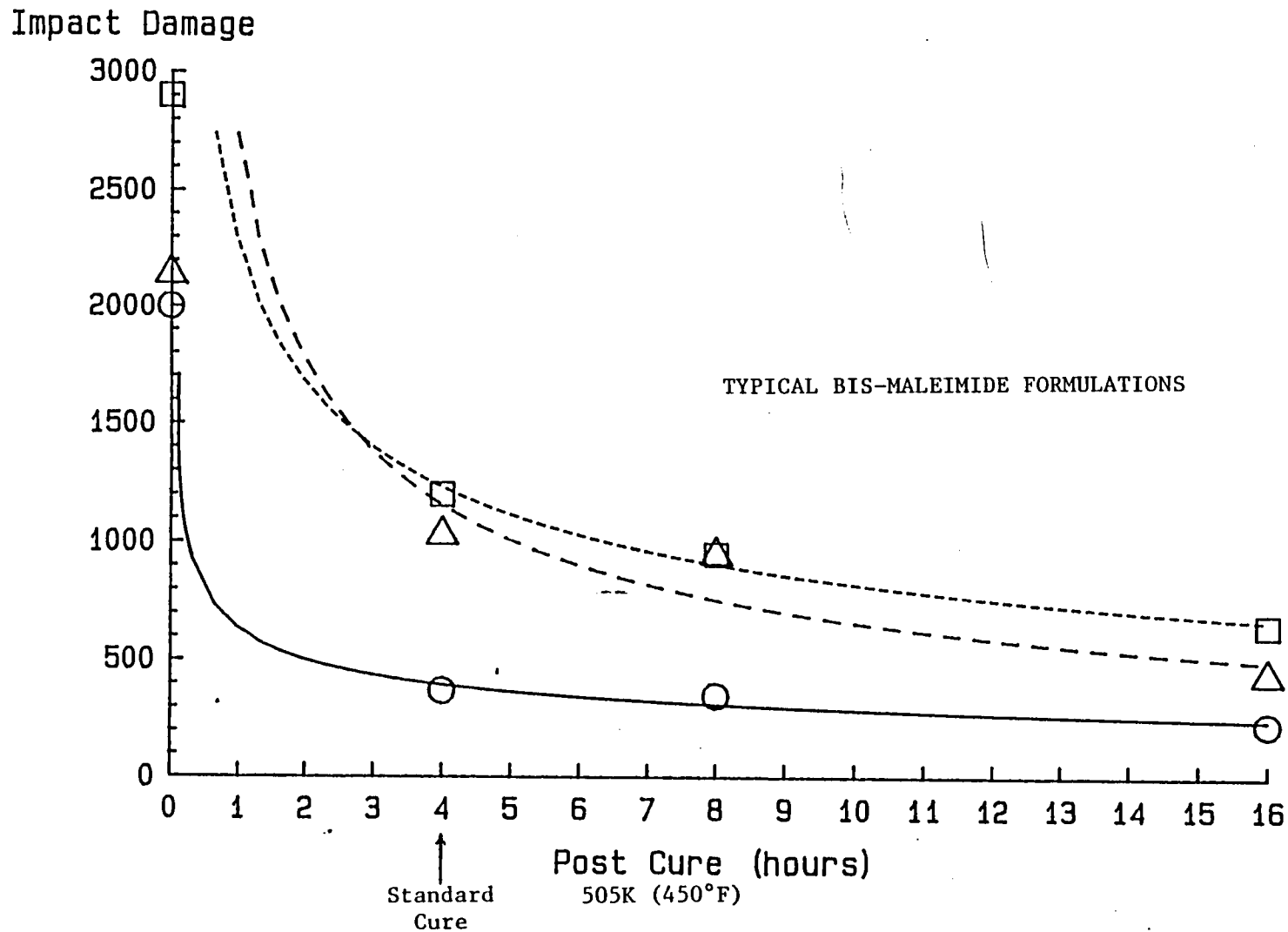
<u>Formulation No.</u>	<u>62</u> 125-21A	<u>63</u> 125-21B	<u>64</u> 125-21C	<u>65</u> 125-21D	<u>66</u> 125-22A	<u>67</u> 125-22B
<u>Resins</u>						
Bismaleimide K-353	25	25	25	25	25	25
XU-276				25		
Epiclon 830	25	25	25	25	35	25
DER 661	25	25	25		20	25
<u>Hardeners</u>						
DDS	7	7		15		5
XU-205				10		20
Anchor 1482	8	8	13.5		15	
<u>Catalysts</u>						
Dicup T		0.6			0.5	0.5
ETTPI	0.3	0.3	0.3	0.3	0.3	0.3
<u>Toughening Agent</u>						
SR-5217A	10	10	10		5	5
<u>Filler</u>						
Cab-o-sil	3	3	3	3	3	3
<u>Gel Time @ 436K</u>	3'15"	3'00"	3'00"	2'45"	5'00"	8'00"
<u>Short Beam Shear Strength (MPa)</u>						
296K (dry)	-	-	57.2	-	73.1	-
366K (dry)	-	-	44.1	-	49.6	-
405K (dry)	-	-	P*	-	P*	-
<u>Impact Resistance</u>	448	685	308	568	438	685

Cure: 2 hr. @ 450K. Postcure: 4 hr. @ 491K.

*P = thermoplastic

FIGURE 1

IMPACT RESISTANCE VS POST CURE BisM/Epoxy Formulations



Power Law Regression Used For Best Curve Fit

CONCLUSIONS

1. Heterogeneous toughening with elastomers is effective in improving the impact resistance of carbon fiber laminates but is achieved at the cost of a significant loss in other mechanical properties. In particular, a severe loss in interlaminar shear properties is observed, especially when hot and wet.
2. Polycarbonate addition results in homogeneous systems with improved impact resistance and this addition also results in significant loss of other mechanical properties. Four parts of polycarbonate per one hundred parts of base resin gives the best results.
3. Molecular weight of the polycarbonate additive did not have a noticeable effect.
4. Cab-o-sil functions only as a flow control agent. In the loading level range investigated it did not have any effect in impact resistance.
5. Diaminodiphenyl sulfone (DDS) was found to be the easiest hardener to use with these types of prepreg formulations. Other aromatic amines such as Uniroyal Tonox gave some improvement in toughness but the amine has such high reactivity that prepregging and handling characteristics were poor.
6. A toughness test which was essentially a Gardner impact test with some special treatment of the damage volume was found to be an effective tool for screening impact resistance. Quantification of the values can be considered to be expressions for the volume of damage suffered by the laminate upon impact.
7. "All epoxy" systems appear to result in better potential for impact resistance while the epoxy-bismaleimides gave better retention of hot and wet strengths with similar formulation changes.
8. A kinetic study revealed several important features of the chemistry of bismaleimides and epoxy blends. These are presented in the report text.
9. Post curing of bismaleimide/epoxy systems beyond the standard 4 hours at 505K results in additional improvement in impact strength.

Appendix A
"All Epoxy" - Formulation #30
Experimental Procedure

Ingredients

DEN 439	11 parts (pts.)
RCI 98-180	4 pts.
MY 720	50 pts.
DDS	21 pts.
Resicure #4	0.3 pts.
Cab-o-sil	4.5 pts.
Lexan	4.0 pts.

Procedure

1. Melt DEN 439 at 394K (250°F).
2. Heat RCI 98-180 to 355-394K (180-250°F).
3. Heat MY 720 to 344-355K (160-180°F).
4. Mix 1, 2, and 3 and stabilize at 350K (170°F).
5. Melt DDS and stir in maintaining mix below 366K (200°F).
6. Cool mix to 316-322K (110-120°F).
7. Adjust viscosity by the addition of a 50/50 mixture of acetone/CH₂Cl₂ to just permit mixing.
8. Dissolve Lexan in 26 pts. CH₂Cl₂.
9. Stir in Lexan solution.
10. Blend in Cab-o-sil with high shear mixer (30 min.).
11. Add Resicure and stir.
12. Adjust solution viscosity by adding 50/50 acetone/CH₂Cl₂ for prepregging.

Appendix B
Bismaleimide/Epoxy - Formulation #10
Experimental Procedure

Ingredients

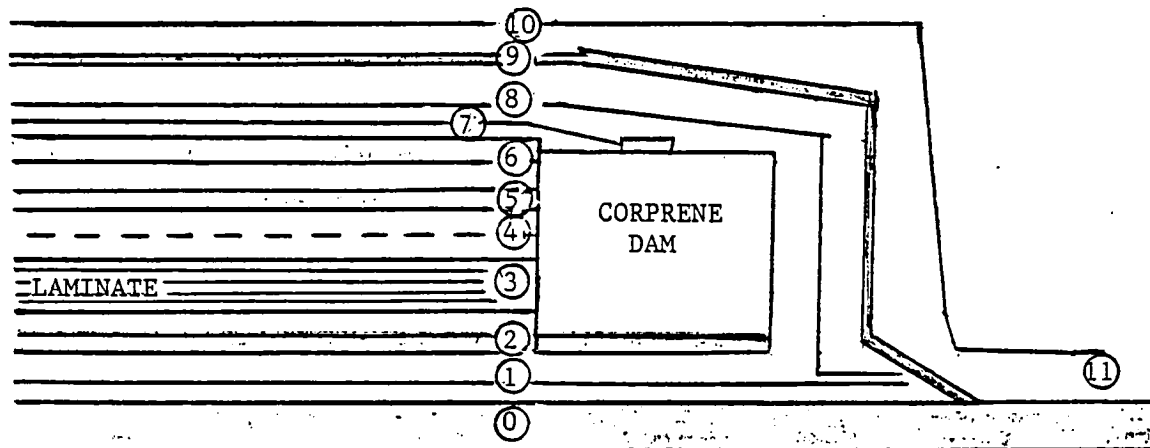
K-353	24 pts.
XU-276	55 pts.
DDS	14 pts.
ETPI	0.3 pts.
Cab-o-sil	2 pts.
ABS	6 pts.

Procedure

1. Preheat K-353 at 394K (250°F) for 90-120 min. to insure complete melting.
2. Preheat XU-276 at 394K (250°F) until completely melted.
3. Melt DDS at 450-477K (350-400°F) until completely melted.
4. Add K-353 to XU-276 at 394K (250°F) and mix until uniform.
5. Cool to ~355K (~180°F) and add DDS (insure that temp. does not get ~366K (>200°F)).
6. Add ABS (in 10% acetone solution) at 333K (140°F) and mix at 333K (140°F) for ~30 min.
7. Add Cab-o-sil under high shear mixing at ~333K (≤140°F) and mix 15-30 min.
8. Add ETPI and keep temp. <333K (<140°F).
9. Cut resin with acetone to prepare for prepregging.

Appendix C
Typical Lamination Procedure

Standard for Dam Layup



- ① 0.64 cm. (0.25 in.) aluminum caul plate
- ② Tedlar
- ③ 0.16 cm. (0.063 in.) aluminum base plate [5.1 cm. (2" larger than the laminate)]
Frekote
- ④ Graphite laminate
- ⑤ TX1040
- ⑥ Bleeder plies (if needed) 120/1581 glass cloth*
- ⑦ 0.16 cm. (0.063 in.) aluminum pressure plate
- ⑧ Tedlar overlapped 1.77 cm. (0.5 in.) onto and taped to corprene dam
- ⑨ Tedlar over entire layup
- ⑩ 2 plies 1581 glass breather
- ⑪ Capran bagging material
- ⑫ Vacuum sealer tape (tacky tape)

Layup Detail

Swatched prepreg on 3K-70P - $42 \pm 2\%$ RC - heat staged ~ 8 min. at 355K (180°F) in oven.

- A. SBS - 0°, 12 ply - 10 cm. x 15 cm. (4" x 6") laminate [cured laminate cut in warp direction to 0.64 cm. x 1.9 cm. (0.25" x 0.75") test specimen]
- B. Impact - 0°, 90°, 0°, 90°, 0°, 5 ply - 15 cm. x 15 cm. (6" x 6") laminate (full cured laminate is test specimen)

		Impact Panel (5 Ply)	SBS Panel (12 Ply)
For Bleeding:	1 ply 1581	5.5% resin bleed	2.3%
	1 ply 120	2.0%	.77%

Cure Schedule:

RT to 450K (350°F)

120 min. @ 450K ($350 \pm 10^\circ\text{F}$)

Increase pressure + 0.31 MPa (45 psi)

Cool to below 333K (140°F) under pressure

BMI/Epoxy Post Cure Schedule:

Cure free standing in oven at 505K (450°F) for 16 hrs. (heat up and cool down should not exceed 3°F/min.)

Appendix D
Glossary of Materials

<u>Material</u>	<u>Comment</u>	<u>Source</u>
<u>Resins</u>		
MY-720	tetraglycidyl derivative of 4,4'-methylene dianiline	Ciba Geigy
Epiclon 830	bisphenol F diglycidyl ether	Dainippon Ink & Chemicals, Inc.
DER 669	glycidyl ether type from bisphenol A	Dow
DEN 439	epoxy novolac	Dow
ERL-0510	triglycidyl derivative of p-aminophenol	Ciba Geigy
XU-276	toughened epoxy	Ciba Geigy
RCI-98-180	epoxy novolac	Reichhold
K-353	bismaleimide	Rhone-Poulenc
Bismaleimide-S	MDA-bismaleimide	Mitsui Toatsu
Bismaleimide-M	tris(p-aminophenyl)methane-maleimide	Mitsui Toatsu
Eponol 855-40	thermoplastic polyether (high M.W.) bisphenol A and bisphenol A diglycidyl ether	Shell
Diacryl 101	bisphenol A ethylene glycol methacrylate	Shell
DEN 661	solid epoxy from bisphenol A	Dow
DER 331	bisphenol A diglycidyl ether	Dow
<u>Hardeners</u>		
DDS	diaminodiphenyl sulfone	Ciba Geigy
LSU 931	DDS adduct (125 epoxy equiv.)	Ciba Geigy
Ancamine 1482	proprietary amine	Pacific Anchor
XU-205	methylene dianiline	Ciba Geigy
<u>Catalysts</u>		
Resicure #4	eutectic of mixed methyl imidazoles	Ozark Mahoning
ETPPI	ethyltriphenyl phosphonium iodide	Aldrich
Dicumyl peroxide	dicumyl peroxide	Hercules
Ancamine 1222	proprietary amine	Pacific Anchor
Dicup T		Hercules

Appendix D cont'd.

Filler

Cab-o-sil (M-5)

Cabot

Toughening Agents

Hydroxyl containing
polyether

Cargill

Hydroxyl containing
polyester 3012A

Cargill

Polycarbonate (Lexan)

General Electric

120

141

101

131

CTBN (I) CTBN 1300 prereacted with an epoxy novolac

Narmco

CTBN (II) CTBN 1300 prereacted with MY-720

Narmco

Photomer 4127 aliphatic difunctional acrylic acid ester

Diamond Shamrock

SR-5217A prereact CTBN and epoxy

Narmco

Hycar 1476 nitrile rubber

Goodrich

Polyether-sulfone GR 200P polyarylene ether sulfone

ICI

Polysulfone UDEL P-1700 polyarylene ether sulfone

Union Carbide

10301 epoxy terminated polyether diamine

Narmco

Reinforcement

Celion 3K-70P woven fabric - 3000 fiber tow - carbon fiber
fabric

Textile Products,
Inc.

Celion 12000 12000 fiber tow - carbon fiber

Celanese

Resin Systems

5208 MY-720 type prepreg resin

Narmco

5240 toughened epoxy resin formulation

Narmco

117M 394K (250°F) curing rubber toughened adhesive

Narmco

3502 MY-720 type prepreg resin

Hercules

934 MY-720 type prepreg resin

Fiberite

Appendix E
Data on Contract Deliverables

TABLE 1
PROPERTIES OF CONTRACT DELIVERABLES

UNITAPE
X126-30-4/C-12K Batch 1074

Physical Properties

Resin Content	36.1%	
Areal Fiber Weight	145.0 g/m ²	
Volatiles	.46%	(325°F/15 min.)
Flow	16.3%	(350°F/100 psi/4 ply)
Gel	10'15"	(350°F)

Appendix E

TABLE 2
PROPERTIES OF CONTRACT DELIVERABLES

UNILAMINATE
X126-30-4/C-12 Batch 1074

	<u>RT</u>	<u>200°F</u>	<u>270°F</u>
<u>0° Tensile</u>			
Strength, ksi	291	285	236
Modulus, msi	25.9	21.6	23.0
Strain, micro in./in.	11,250	12,500	10,250
<u>0° Compression</u>			
Strength, ksi	249	147	118
24 hr. water boil		114	77
<u>0° Flex</u>			
Strength, ksi	220	187	166
Modulus, msi	16.6	16.6	17.1
<u>Short Beam Shear</u>			
Strength, ksi	17.2	12.8	11.1
Dry		8.2	8.8
Wet			
8 Ply Panel		16 Ply Panel	
(For tensile, compression, flex)		(For short beam shear)	
Cured % RC	32.5	35.8	
Fiber volume, %	60.9	57.0	

Appendix E

TABLE 3
PROPERTIES OF CONTRACT DELIVERABLES

FABRIC LAMINATE
X126-30-4/3K 70 PB

		<u>RT</u>	<u>200°F</u>	<u>270°F</u>
<u>Compression</u>				
Strength, ksi		83	74	76
24 hr. boil			48	40
<u>Flex</u>				
Strength, ksi		96	100	93
Modulus, msi		7.1	7.0	6.8
<u>Short Beam Shear</u>				
Strength, ksi	Dry	11.1	9.9	8.4
	Wet		7.9	6.5
12 Ply Panel				
Cured % RC		41.3		
Fiber volume		50.6		

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16. Abstract This contractual effort was directed towards the study of factors which effect the impact resistance of laminating resin systems and yet retain equivalent performance with the conventional 450K (350°F) curing epoxy matrix systems in other areas. Formulation work was conducted on two systems, an all-epoxy and an epoxy/bismaleimide, to gain fundamental information on the effect formulation changes have upon neat resin and composite properties. The all-epoxy work involved formulations with various amounts and combinations of eight different epoxy resins, four different hardeners, fifteen different toughening agents, a filler, and a catalyst. The epoxy/bismaleimide effort involved formulations with various amounts and combinations of nine different resins, four different hardeners, eight different toughening agents, four different catalysts, and a filler. When a formulation appeared to offer the proper combination of properties required for a laminating resin (e.g. melt impregnable, reasonable working time, tack, etc.), Celion 3K-70P fabric was prepregged. Initial screening tests on composites primarily involved Gardner type impact and measurement of short beam shear strengths under dry and hot/wet conditions.					
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